

# A TRIDENT SCHOLAR PROJECT REPORT

NO. 242

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"INVESTIGATION OF ION TRANSPORT MECHANISMS IN NAFION IN THE  
PRESENCE OF WATER AND METHANOL"

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ANNAPOLIS, MARYLAND

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PRESENCE OF WATER AND METHANOL"**

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## ABSTRACT

The electrical conductivity of NAFION membranes in various methanol/water solutions was measured. The conductivity measurements were conducted at frequencies between 100 Hz and 40 MHz while the membrane was at room temperature and atmospheric pressure. The membranes absorbed different amounts of each solution by either soaking in the solution, being suspended over the solution, or being given a small amount of solution to absorb while in a closed tube. Generally, it was found that membranes with a high methanol fraction did not have high conductivity. The highest conductivity was found in pure water samples. This led to the conclusion that at these concentrations, methanol does not significantly affect the conductivity of protons but does pass through the membrane. Solutions with a small amount of methanol appeared to be absorbed more by the membrane than did pure water. This may be due to the larger mass of the methanol molecule. The large amount of methanol absorbed by NAFION in this experiment is indicative of methanol crossover.

**Keywords:** NAFION, methanol, water, conductivity, conduction mechanisms

## TABLE OF CONTENTS

1. Introduction	p.3
2. Theory	p.5
2.1 Fuel Cell Theory	p.5
2.2 Fuels	p.6
2.3 NAFION Membrane	p.6
2.4 Impedance Measurements	p.8
3. Experimental Methods	p.12
3.1 Preparation	p.12
3.2 Immersed Conditioning	p.13
3.3 Suspended Conditioning	p.13
3.4 Controlled Exposure Conditioning	p.13
4. Results	p.15
4.1 Experimental Results	p.15
4.2 Analysis of Results	p.17
4.3 Conclusions from Results	p.20
4.4 Uncertainty	p.21
5. Conclusion	p.22
6. Future Work	p.24
7. Tables and Figures	p.25
References	p.43
Appendix A- Error Analysis	p.44

## INTRODUCTION

Environmental concerns have become increasingly important to today's society. Environmental groups, such as Greenpeace and the Sierra Club, have been pushing lawmakers and society into being more environmentally conscious. Among the measures lawmakers have passed in support of cleaning up our environment, have been several on controlling transportation emissions. Studies of our current modes of transportation have shown that their emissions have deleterious effects upon our atmosphere. The internal combustion engine used to run most vehicles emits several byproducts which have been proven to harm not only plants and animals, but our entire environment.

Consequently, researchers have been searching for an alternative to the combustion engine. Electric and solar powered vehicles have proved to have a number of limitations although they are much less harmful to the environment. Solar vehicles can only be driven while the sun shines or must rely on a battery for backup power. Electric vehicles also rely on batteries, which need to be recharged far too often for convenience. Also, conventional batteries are difficult to dispose of because of the hazardous chemicals they contain. Yet, using a chemical reaction to create electricity can be one of the most efficient and harmless ways of producing power.

Does this alternative exist? It has since 1839, when Sir William Grove created what he called the fuel cell [1]. It utilized reverse electrolysis of hydrogen and water to create electricity. However, his device was not capable of delivering enough power to make it useful, and so it received little attention for the next century. Finally, in the late 1960's, NASA needed a portable electrical power source that did not rely on sunlight or atmosphere

to power its Gemini and Apollo space missions. After finding that the fuel cell was what they needed, they funded a large research program to further develop it. Although this program foundered after a few years, through it the fuel cell gained recognition for its potential higher efficiency, power density, and lack of environmentally harmful byproducts. The military has also shown a great deal of interest in using the fuel cell. Its silence and low infrared signature make it ideal for use in submarines and other vehicles. Due to the combined interest of all these parties, research in recent years has been escalating [1].

Currently five types of fuel cells exist: alkaline, proton-exchange membrane, phosphoric acid, molten carbonate, and solid oxide ceramic [1]. These types are distinguished by their electrolytes and possess different operating characteristics. The proton-exchange membrane fuel cell is the variety used in NASA's Gemini missions. It can operate at atmospheric pressure and temperature conditions, which make it particularly desirable for everyday use. Currently, a proton-exchange fuel cell is being tested in buses in Vancouver, British Columbia [2]. However, there are still a few problems inherent in creating economically and publicly viable proton-exchange membrane fuel cells. One major problem is the lack of good proton-exchange membranes. Currently the best membrane is NAFION<sup>1</sup>, a cousin of TEFLON. While NAFION possesses many of the characteristics desired for an electrolyte, it also has a few problems. These problems will be discussed in more detail in Section 2.3. Research has been focussing on NAFION's conduction mechanisms in order to aid researchers interested in solving its problems. This project aims to contribute to this effort.

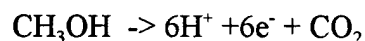
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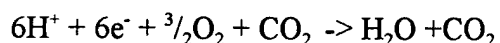
## THEORY

### 2.1 Fuel cell theory

Fuel cells use an injected fuel to create an electric current. The main components are a porous anode, a porous cathode and an electrolyte (Fig 1). The fuel, which in principle can be any substance capable of dissociating, is injected into the anode. If methanol is used as an example fuel, it dissociates upon contact with a catalyst with the reaction:



In a proton-exchange membrane fuel cell the perfect electrolyte forms a barrier to electrons and fuel, but is permeable to protons ( $\text{H}^+$ ). Protons then enter the cathode into which an oxidant (normally oxygen) has been injected. Electrons must pass through an external circuit into the cathode, thereby creating an electric current. In the cathode, the protons, electrons and oxidant combine to make water and heat in the reaction:



Depending on the engineering of the cell, the byproducts created from these reactions, water and carbon dioxide, may be removed from the cell. Because a fuel cell does not rely on a cyclically operating heat engine to create the electrical current, its efficiency,  $\eta$ , depends on the heats of reaction of the fuel, and the energy of the electrons created in the reaction. The efficiency thus becomes:

$$\eta = \frac{\Delta G_T}{\Delta H_o} \quad \text{Eq [1]}$$

where  $\Delta G_T$  is the change in free energy of the electrons at the operating temperature  $T$ , and  $\Delta H_o$  is the heat of combustion of the fuel [1].



## 2.2 Fuels

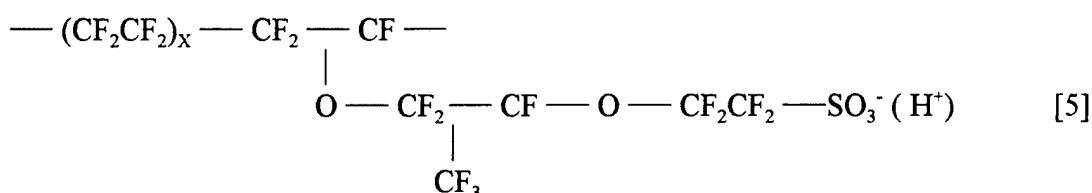
Many different substances may be used as fuels. Hydrogen has so far been the fuel of choice because it has a very high electrochemical reactivity, and its reaction mechanisms are very well understood [1]. Hydrogen allows a maximum ideal efficiency of 83% [1]. However, it is expensive, explosive, and does not exist as a liquid in atmospheric conditions, making it difficult to store. Because of this, hydrogen poses problems for portable fuel cells such as those used for powering vehicles. Another substance which is receiving attention as a possible fuel is methanol. Methanol is not only relatively cheap, but exists as a liquid at room temperature, and is thus easy to handle. It has been used mostly in acid electrolytes (such as polymer-exchange membranes) because it is not as reactive as hydrogen. While methanol can optimally produce a higher maximum ideal efficiency, 97 % [1], its low reactivity requires catalysts such as platinum or platinum alloys within the electrode to begin the reaction. Methanol has a molecular weight of 32 g/mol, making it a heavier molecule than water. It also has a vapor pressure of 97.25 mmHg which is higher than that of water, 17.55 mmHg [3].

## 2.3 NAFION Membrane

The proton-exchange membrane fuel cell typically uses a polymer as its electrolyte. This polymer's main function is to transport protons between the anode and cathode. A perfect membrane must have high proton conductivity, no electronic conductivity and may not conduct the fuel molecules [1].

One polymer currently being used as an electrolyte, NAFION, is the best of these polymers to date, but it still does not possess some of the key attributes of a perfect

electrolyte for a methanol fuel cell. NAFION was developed by Dupont in 1968 [1]. It is a copolymer of tetrafluoroethylene and perfluorosulfonylethylvinylether [4], whose chemical structure looks like this:



It is composed of a fairly rigid backbone indicated by the  $\text{--(CF}_2\text{CF}_2\text{)}_x\text{--CF}_2\text{--CF--}$  groups shown above. Attached to that backbone are side chains, which terminate in  $\text{SO}_3^-$  groups. These side chains are able to interact with ions and are the reason NAFION transports protons very well. However, this conduction only occurs efficiently when the polymer has been hydrated [5].

Researchers do not yet fully understand the conduction mechanisms of NAFION, although several models of these mechanisms have been proposed. The model currently accepted by most researchers is that protons surround themselves with several clusters of water molecules, which then interact with the side chains of the polymer. When the proton is transported through the membrane, the side chains flex so that the proton jumps from one side chain to another, dragging its water molecules with it [4,5]. This model has found to be fairly accurate when small amounts of water are present within NAFION. Another model is that the backbone of the polymer itself flexes to allow the proton passage. This method of conduction is more likely to occur with a high water content because larger parts of the polymer must flex, which is easier to do in an aqueous environment [6]. These models explain why NAFION is only conductive when hydrated.

Previous research performed by Zawodzinski et al. has also theorized that NAFION possesses a methanol crossover problem which means that NAFION does not completely block methanol transport but lets some pass through [7]. This phenomenon can greatly decrease the efficiency of the fuel cell. Few studies have been performed to determine the conduction mechanisms when the polymer is surrounded by both methanol and water, although this would be the situation in a fuel cell. In this study the conductivity of NAFION following exposure to different concentrations of water and methanol mixtures will be measured in an attempt to further develop the conduction mechanism models.

#### **2.4 Impedance Measurements**

Measuring the ionic conductivity of a non-metallic substance is very similar to measuring the electronic conductivity of a metal. However, although a DC voltage source may be used to measure the conductivity of electrons in a metal, a phenomenon known as space charge is frequently created when performing the same measurement with ions in a substance. Space charge occurs when ions pile up at the electrodes. This creates a false impression of the conductivity of the sample.

Instead of a DC voltage, an AC voltage source may be applied to the sample. The proton is then pushed back and forth within the sample so the space charge phenomenon can be avoided. However, if the frequency is too low, ions will again gather at the electrodes, creating the space charge problem. If the frequency is too high, ions cannot move through the sample quickly enough, and the conductivity of the sample decreases to zero. Since different substances have different frequency characteristics, one way to characterize the conductivity of the sample is by varying the frequencies of the AC voltage applied to the

sample.

The actual electrical response of a sample is rather complicated. The bulk resistivity cannot be determined outright. Instead, a model must be developed to explain the different responses to the voltage. The measuring device compares the response of the sample to a standard resistor and capacitor in parallel. The test resistor and capacitor values are changed until their response matches the response of the sample at that frequency. Impedance theory indicates that the complex impedance of a resistor and capacitor in parallel is calculated to be:

$$\frac{1}{Z^*} = \frac{1}{R} + \frac{1}{j/\omega C}$$

where  $Z^*$  is the complex impedance of the sample,  $R$  is the bulk resistance,  $\omega$  is the frequency of the ac voltage, and  $C$  is the capacitance of the sample. Rearranging for  $Z^*$  the equation becomes:

$$Z^* = \frac{R + j\omega R^2 C}{1 + \omega^2 R^2 C^2}$$

$Z^*$  may be split into its real and imaginary components:

$$Z^* = Z' + Z''j$$

The real component becomes:

$$Z' = \frac{R}{1 + \omega^2 R^2 C^2} \quad \text{Eq [2]}$$

And the imaginary component is:

$$Z'' = \frac{j\omega R^2 C}{1 + \omega^2 R^2 C^2} \quad \text{Eq [3]}$$

This model would give rise to a semi-circle with radius  $R/2$  on a complex impedance plot, as can be seen in Figure 2. Also shown in Figure 2 is a straight line on the low frequency

side of the plot. This line is the result of an equivalent blocking capacitor, a capacitor

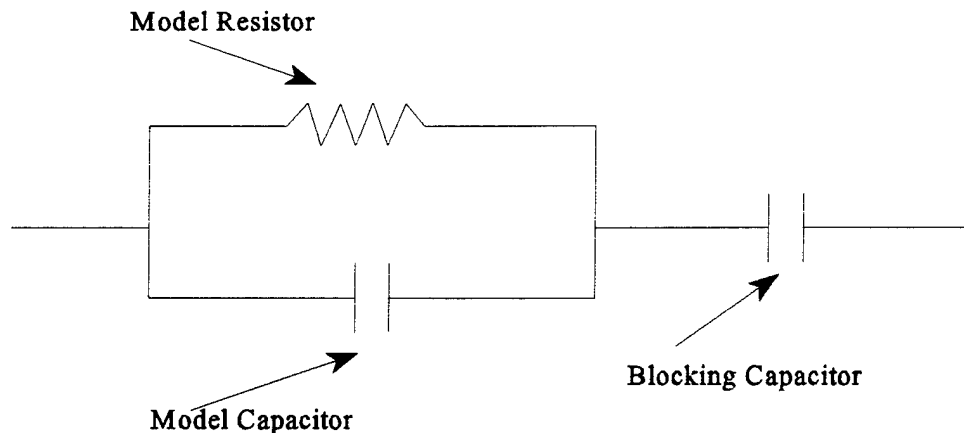


Diagram of the equivalent circuit measured by the HP-1492-A Complex Impedance Analyzer

which is placed in series with the modelled resistor-capacitor parallel circuit. This blocking capacitor term appears because electrodes on each end block the protons from leaving, resulting in a response which can be approximated by a series capacitor.

To determine the conductivity of a sample, the instrument measures the equivalent real and imaginary impedances of the sample, and by graphing the real versus the imaginary component, the bulk resistance,  $R$ , of the sample can be determined by finding the x-axis intercept of the graph. The conductance,  $G$ , is simply the reciprocal of  $R$ :

$$G = \frac{1}{R} \quad \text{Eq [4]}$$

The conductivity of the sample is then calculated:

$$\sigma = \frac{l G}{A} \quad \text{Eq [5]}$$

$\ell$  is the length of the sample between the electrodes,  $A$  is the cross-sectional area of the sample ( the width times the height) and  $\sigma$  is the electrical conductivity of the sample.

A sample impedance plot for a NAFION membrane which has been exposed to a mixture of water and methanol is shown in Figure 3. This impedance measurement, like all in this project, was measured by the Hewlett-Packard 1492-A Impedance Analyzer. The HP 1492-A is capable of measuring impedances at frequencies from 100 Hz to 40 MHz. The semicircle on the plot is slightly depressed, and the straight line is no longer straight. These variations did not have any bearing upon this research because the only data used from this plot was the x-axis intercept [8]. Since this intercept did not always actually intercept the x-axis, the lowest point on the semicircle was used to determine  $R$ .

## EXPERIMENTAL METHODS

### 3.1 Preparation

There are many different forms of NAFION. However, NAFION 117 was used for this project. The 117 designates an equivalent molecular weight of 1100 g/mol, and a thickness of 0.017 cm. The polymer was obtained from DuPont. Prior to use in these experimental runs, the polymer was pretreated in the USNA Chemical Laboratory. It was boiled in a 3% solution of hydrogen peroxide for one hour, washed in boiling water for one hour, and soaked in boiling 1:20 dilute solution of sulfuric acid for one hour [9]. This procedure is used to ensure that no extraneous ions are attached to the side chains, and is standard practice when NAFION is used [9]. It was then placed in deionized water for storage until use.

The samples were approximately 4 cm long. The ends of each sample were sputtered with a gold film (thickness  $\sim 10$  nm) within a vacuum, thus creating a distance between the electrodes,  $l$ , of approximately 3 cm. The samples were subsequently placed in a dry box, where the humidity was less than 10%, for two to three days. This ensured that all remaining deionized water was evaporated from the NAFION. Mixtures of water and methanol were prepared by volume. For example, a 3:1 mixture consisted of 3 times as much volume of methanol as of water. The solutions were prepared in the following ratios: (Methanol : Water) 1:0, 4:1, 3:1, 2:1, 3:2, 1:1, 2:3, 1:2, 1:3, 1:4, 0:1. These mixtures were placed in glass jars of diameter 3 inches, as seen in Figure 4. The jars were closed with air tight lids made of plastic. Alligator clips with leads attached were fed through the lids, and epoxied on to ensure air tightness. These constituted the connection for the samples. Three different

methods of conditioning the sample with the mixture were used to vary the amount of solution taken up as much as possible.

### **3.2 Immersed Conditioning**

The dimensions and weight of a NAFION sample of approximately 1 cm width were measured within the drybox. The sample was then removed from the drybox, and immediately placed in one of the solutions contained within the jars. It remained there for one hour, at which point it was removed from the solution and weighed in a Sartorius scale with a precision of 0.0001 gms. It was then immediately attached to the alligator clamps which suspended it above the solution in the jar, and an impedance measurement was made. The sample's exposure to the room atmosphere was made as small as possible, so the dimensions of the sample were not directly measured for this procedure. They were calculated by interpolating from the suspended sample's percent weight uptake and percent dimension change.

### **3.3 Suspended Conditioning**

The previously immersed sample remained suspended over the solution and was allowed to equilibrate in the atmosphere of that jar, at room temperature,  $T = 20^{\circ}\text{C}$ , for 24 hours. At the end of the 24 hours, another impedance measurement was taken. The dimensions and weight of the sample were remeasured as quickly as possible so as to minimize the exposure to room atmosphere.

### **3.4 Controlled Exposure Conditioning**

The third method used for conditioning the NAFION consisted of placing a sample of width 0.5 cm in a length of "PharmEd" tubing from Cole Parmer which had an inside radius



of 1/4 inch. This tubing was inert with regard to methanol, water and NAFION. Stainless steel electrodes were inserted at each end of the tube, one end in contact with the sputtered gold ends of the sample with the other end exposed to the atmosphere. The tube was then sealed off from the atmosphere by clamping down on both ends. This preparation took place within the dry box. The sample's weight and dimensions were measured prior to its insertion in the tube. Using a syringe, approximately 30% of the sample's weight of solution was injected through the clamp into the tube. The amount of mixture was calculated by using the density of the mixture and the original, dry, weight of the sample. The density of the mixture was calculated to be:

$$\rho(\text{mixture}) = F(\text{meth})\rho(\text{meth}) + F(\text{water})\rho(\text{water})$$

where  $F$  is the fraction of methanol or water present within the mixture. The density of methanol at room temperature,  $T = 20^\circ \text{C}$ , was taken to be  $.791 \text{ g/cm}^3$  and the density of water at room temperature was taken to be  $1 \text{ g/cm}^3$  [6].

The volume to be injected was then calculated by:

$$V(\text{mixture}) = \frac{(0.3) w_i}{\rho(\text{mixture})} \quad \text{Eq [6]}$$

where  $V$  is the volume of the mixture, and  $w_i$  is the original weight of the sample when it was dry. The sample was allowed to equilibrate for 24 hours. The leads from the Complex Impedance Analyzer were then attached to the steel electrodes, and an impedance measurement was performed. Immediately after this measurement the sample was removed from the tube. Its weight and dimensions were measured immediately afterwards, again reducing the effects of exposure to room atmosphere.

## RESULTS

### 4.1 Experimental Results

Three different methods of conditioning the samples were used to ensure that as broad a range as possible of the samples' reactions to the conditioning was observed. Each of these methods resulted in a different percent uptake of solution, depending on the solution. As seen in Table 1, immersed samples attained the greatest amount of uptake, while suspended samples absorbed a smaller amount of solution than immersed samples. The controlled conditioning samples resulted in a spread of percent weight uptakes from 15% to 45%. The percentage of solution taken up was calculated by:

$$\% \text{Weight Uptake} = \frac{(W_f - W_i)}{W_i} \times 100 \%$$

where  $W_f$  is the weight of the sample after conditioning and  $W_i$  is the initial, dry weight of the sample. The volume of solution present was also calculated:

$$V(\text{uptake}) = \frac{M(\text{uptake})}{\rho(\text{mixture})} \quad \text{Eq [7]}$$

where  $V$  is volume,  $\rho$  is density, and  $M$  is mass. The weight of water and weight of methanol present within the sample could then be found to be:

$$\begin{aligned} W(\text{H}_2\text{O}) &= V(\text{uptake})F(\text{H}_2\text{O})\rho(\text{H}_2\text{O}) \\ W(\text{meth}) &= V(\text{uptake})F(\text{meth})\rho(\text{meth}) \end{aligned} \quad \text{Eq [8]}$$

When the membrane was in direct contact with the solution, it was assumed that methanol and water entered the membrane in the same ratio as was present within the solution, based on a study by Zawodzinski et al [8], who showed that this happened because

the ratio of the NMR signal strengths was equal in the solution and the sample. The controlled conditioning samples absorbed all of the solution injected into the tube, which is consistent with Zawodzinski's findings. Therefore in these conditioning methods, the proper ratio of methanol to water was maintained. However, in the suspended method, the sample was in contact with the atmosphere produced by the mixture. Since methanol has a higher vapor pressure than water, more methanol could be present within the atmosphere, thus creating a change in the methanol/water ratio absorbed by the sample. However, upon graphing the conductivities of the immersed and controlled conditioning data versus the percentage of solution absorbed and comparing it to the suspended data, no large tendency towards a heavier methanol concentration was seen. This is shown in Figure 5, where the suspended data for a 4:1 and a 1:4 mixture is shown in filled squares and filled circles respectively, while the other two methods are shown in open squares for 4:1 and open circles for 1:4. The suspended data falls along the same general line as the controlled and immersed data. If the amount of methanol present within the suspended membrane were greater than that found in either the controlled or the immersed membrane, the conductivity would be lower, while the percentage of weight absorbed would be higher.

Previous studies have shown that a maximum amount of solution is taken up when NAFION is directly placed within the solution [10]. Because the conductivity of the solutions themselves was extremely high, the samples could not be placed directly within the solutions to be measured. It was therefore necessary to remove the sample from the surrounding solution after conditioning to obtain an accurate impedance measurement. It was determined through observation that one hour was enough time for the sample to reach an equilibrium

stage with a maximum uptake of solution.

All suspended samples absorbed a markedly smaller amount of solution. This is known as Schroeder's paradox [10], which happens in many polymers conditioned with solvents. It has not been determined why this occurs, and as this phenomenon had no direct bearing on the results of this experiment, it was ignored.

Since immersing the sample and suspending it allowed the sample to determine how much solution was taken up, a method was devised to control the amount of solution entering the sample. Both prior methods were found to have percent weight uptakes ranging from 30% by weight for high water content to 60% by weight for high methanol contents, so an approximate amount of 30% of the solution was used as the control. This method resulted in a spread of uptakes centered on 30%.

#### **4.2 Analysis of Results**

All methods of conditioning the NAFION showed consistent general trends. As the water content of the solution increased, the conductivity of the samples increased, but less solution was absorbed by the sample. As the methanol content increased, the conductivity increased a small amount, and more solution was absorbed. Figures 6 through 10 show these trends for various solutions. The conductivity is plotted versus the percent weight uptake for each different solution. An error analysis was done for one of the data points, and this point is shown with average error bars. Appendix A discusses this in more detail.

Figure 6 shows pure water and methanol data. The samples treated with pure methanol were found to have the lowest conductivities. These conductivities also remained fairly constant. This is explained by the fact that methanol is less polar than water. It does

not dissociate easily and therefore does not interact as strongly with protons. Methanol also seems to be taken up in greater weight quantities. This is partially explained by the fact that methanol has a molecular weight of 32 g/mol, while water only has a molecular weight of 18 g/mol. Regardless, the indication that methanol is taken up by NAFION in large quantities is indicative of a methanol crossover problem, which occurs when methanol enters the sample and transports through it.

The samples conditioned with pure water are found to have much higher conductivities, but lower percent weight uptakes. Zawodzinski et al have determined that the electroosmotic drag coefficient (defined by Zawodzinski as the number of water molecules per  $H^+$  transported across the membrane sample) of NAFION is approximately 2.5 [10]. This means that one proton surrounds itself to approximately three water molecules, which in turn interact with the side chains. As the side chains move, the protons with their surrounding water molecules come into contact with other side chains, allowing the protons to move through the polymer. This theory accounts for the conductivity increasing rapidly with increasing water content in the membrane. With a low water content, this process is limited.

Figures 7 through 10 each show the results of NAFION being exposed to several different solutions (e.g., 2:1 and 1:2 solutions are present on the same graph with water and methanol). They all present the data from the pure water and methanol solutions for comparison to the mixed solutions. These graphs show that solutions with more methanol present have lower conductivities and that an increased amount of solution causes a lesser change in the conductivity than those with more water. Therefore, the results shown here agree with the previous theories regarding the roles of methanol and water in the conduction

of protons. Figure 10 shows the data from samples conditioned with the 2:3, 3:2, and 1:1 solutions. In the first three graphs, the data points of the various solutions range largely in between those of pure water and methanol. To remain in agreement with those results, the data points from the solutions with the least difference in the methanol/water ratio should also logically lie in the middle of the graph. However, they show a greater variance in weight uptakes and conductivities than the solutions with a marked difference in the amount of methanol and water. Their trends lie only very generally in the plausible regions indicated by the other solutions, between the data from water on one hand and methanol on the other. More data will have to be taken in this area before a concrete conclusion regarding these solutions can be formed.

Another graph of interest is Figure 11. The log of the conductivity has been plotted versus the log of the percent weight uptake for pure water and pure methanol. The open squares are data from a previous experiment of Wintersgill and Fontanella [11]. This extra data was used for comparison to the data in this experiment. The filled in squares indicate the pure water data taken in this experiment, and show good agreement with the previously taken data. The trend of this graph is towards an asymptotic maximum conductivity, which occurs when large water concentrations are present within the sample. When a large amount of water is present within NAFION 117, more water molecules are present than the three needed for proton conduction. Consequently, instead of interacting closely with the side chains of the polymer, the protons move through regions of high water content within the polymer. These regions of high water content have a higher conductivity than that of the polymer, and since there is no substance present which has a higher conductivity, this creates a maximum

The methanol data (filled circles) appears to reach a much smaller maximum conductivity relative to water. This is not surprising since, as stated earlier, methanol is less likely to interact with protons than is water. In fact, the overall picture of conduction within the polymer when pure methanol is present should present a much flatter curve than when water is present. Since only the maximum conductivity was measured in this project, this theory can not yet be proven. Since the model of the conduction mechanism changes as the amount of water changes, no one curve may be fit to the data.

Figures 12 through 17 show the total amount of weight taken up by the sample as well as the amount of water weight taken up for samples from solutions of 1:4, 1:3, 1:2, 2:1, 3:1, and 4:1. Solutions with a high water content show that the amount of water present within the sample is not greatly affected by the amount of methanol, and that the conductivity is not affected by methanol. The solutions with greater amounts of methanol, 4:1, 3:1, 2:1, show a smaller overall conductivity. However, when only the conductivity of the amount of water present within the sample is examined, it remains on the curve given by the data from Wintersgill and Fontanella [11]. When smaller amounts of methanol are present, as is the case in solutions of 1:4, 1:3, and 1:2, the conductivity of the entire solution lies only a small distance below that of the pure water data.

#### **4.3 Conclusions from Results**

From the data analyzed above, water remains the primary contributor to the conduction of protons. The conduction produced by water molecules is not strongly influenced by methanol in the range of conditions seen in this project. Adding methanol to water in the membrane does not aid the conduction of protons produced by the presence of

water, nor does it help water enter the membrane in greater amounts. It also does not significantly hinder the conduction of protons. Since methanol is clearly absorbed by NAFION in substantial amounts, methanol crossover occurs.

#### **4.4 Experimental Uncertainty**

The data from this project shows considerable scatter (See Appendix A). While general trends were observed, detailed analysis of these trends was not possible due to this large uncertainty. The spread from these data points appears from several uncertainties that were present while measuring the samples. First, the exposure to the room's atmosphere may have caused samples to dry when they were weighed and measured. Although every effort was made to ensure that this exposure was as brief as possible, it did occur. This problem could be solved if a closed container (such as a glove box) were allowed to equilibrate to the atmosphere of the solution. The samples could then be weighed and dimensioned in that container. Another uncertainty was caused by solution remaining on the polymer's surface. Since the polymer was allowed to absorb the maximum amount of solution, there was often extra moisture present on its surface. This moisture was blotted off, but some may have been missed, causing uncertainty in the weight measured. Other uncertainties may have been introduced by bad contacts with the polymer's electrodes, creating false complex impedance graphs. Systematic error, in measuring the resistivity of the sample from the complex impedance graphs, as well as timing the exposure of the samples, and measuring the dimensions, also created uncertainty. While much of this error could not be minimized due to the conditions in which these experiments were performed, taking a larger number of data points could show more conclusive trends.



## CONCLUSION

It has been shown both in this project and in other work [7] that NAFION has a methanol crossover problem. Although NAFION is a very good proton conductor, its problem with methanol transport will hinder its usefulness as the electrolyte in fuel cells. Researchers trying to develop solutions to this problem have tried several different methods. Some of these methods include: hindering the transport of methanol by thickening the polymer, making it more difficult for methanol to transport through; doping the polymer with methanol resistant substances; or adding a methanol resistant layer to the polymer. Through the knowledge of NAFION's conduction mechanisms gained in this experiment and many others, scientists can also begin developing new polymers that do not possess a methanol crossover problem, but still conduct protons very well.

Another problem inherent with using NAFION as an electrolyte is that water must be present for the high proton conduction needed in the fuel cell. This could create fuel cell engineering problems. The water present in the membrane should be enough for the membrane to absorb the maximum amount, but not so much that water crosses over to the anode and dilutes the methanol fuel. Consequently, the water created in the cathode of the fuel cell will have to be carefully monitored to ensure that this anode flooding does not occur.

The problems with developing a good electrolyte are not the only ones plaguing the development of a commercially viable fuel cell. Different fuels are being investigated. Problems creating a large enough anode/fuel interface have been encountered. The catalyst often poisons the cathode, making the production of water difficult, and the overall engineering of the cell has been discovered to be much larger than convenient for portability.

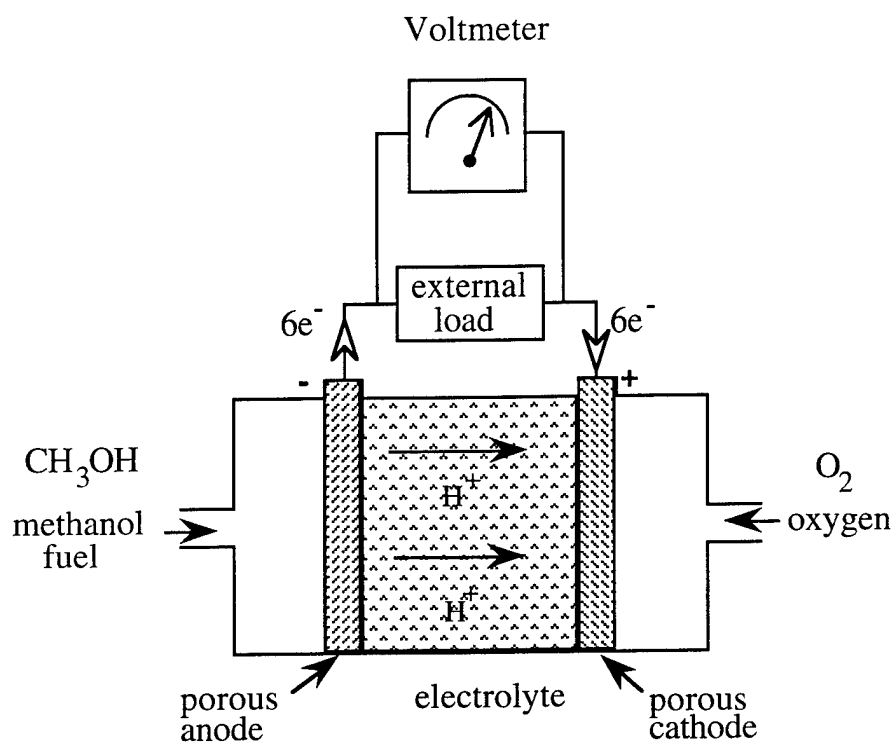
However, with the continued emphasis on development and problem solving, the fuel cell will soon be an integral part of our society. Its potential is far too great for it to be ignored any longer.

## **FUTURE WORK**

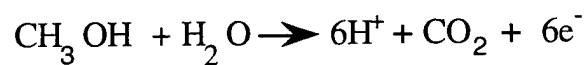
While this experiment provides a good experimental data set which can aid the development of further ion transport models, it does not provide a complete view of the processes involved. A complete theoretical model may be developed by performing the same experiment and varying other variables, such as the pressure, temperature, and molecular weight of the sample. Varying the pressure will aid in finding a value for the activation volume of the conduction mechanisms. Varying the sample's temperature will aid in determining the activation energy needed for proton transport, while varying the molecular weight of the sample will show a clearer picture of the contribution of the backbone of the polymer to conduction. NMR measurements may also be performed to obtain information on the short ranged motion within the polymer. All of these experiments together will form a detailed view of the conduction mechanisms of NAFION, and aid researchers in forming a complete set of models of ion transport within this polymer.

Solutions	Percent Weight Uptake		
	Immersed	Suspended	Controlled
1:0	63.7	56.1	34.9
4:1	61.3	49.3	43.8
3:1	52.7	37.0	36.9
2:1	52.4	37.0	44.6
3:2	51.9	37.4	26.5
1:1	50.6	40.3	21.1
2:3	46.3	43.3	21.0
1:2	42.1	39.6	42.9
1:3	34.2	26.5	24.9
1:4	35.7	33.0	35.6
0:1	33.1	20.6	21.1

Table 1: Weight percent uptake for each solution with the three methods of conditioning



Anode reaction



Cathode reaction

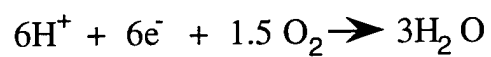


Figure 1: Schematic Diagram of a methanol fuel cell

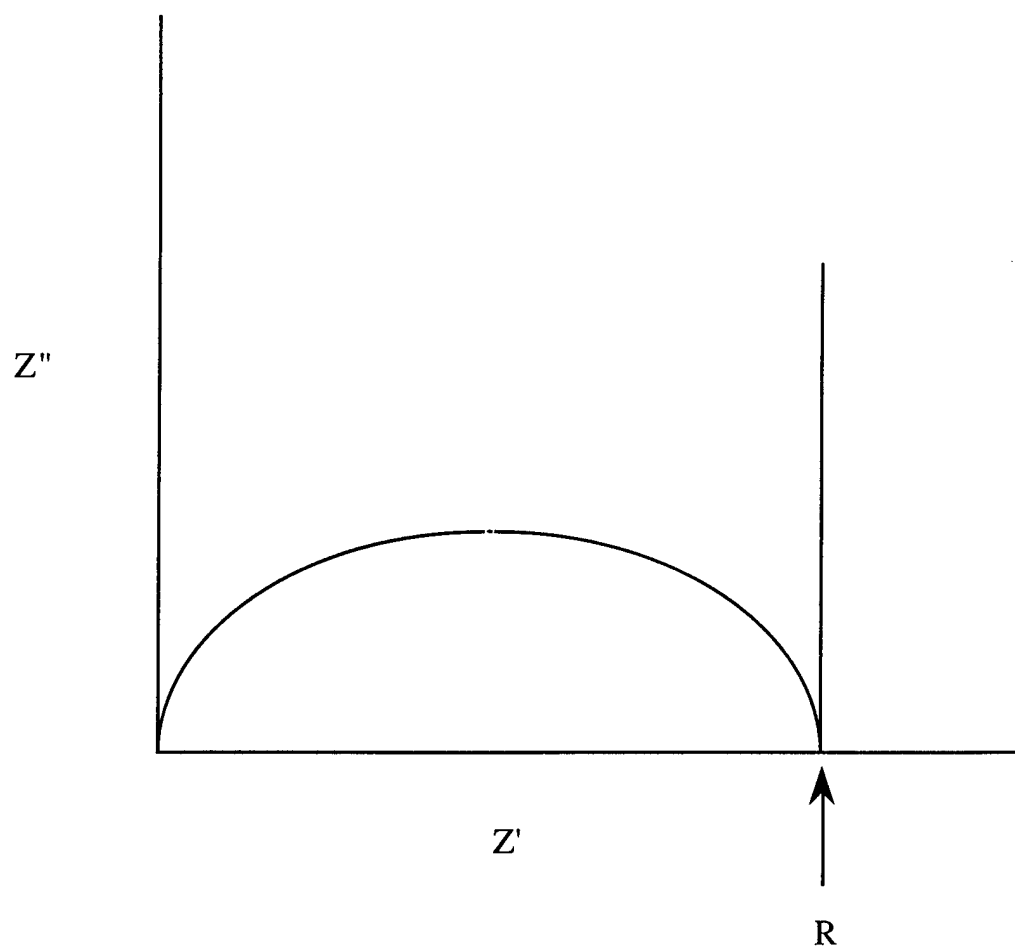


Figure 2: Theoretical Complex Impedance Plot

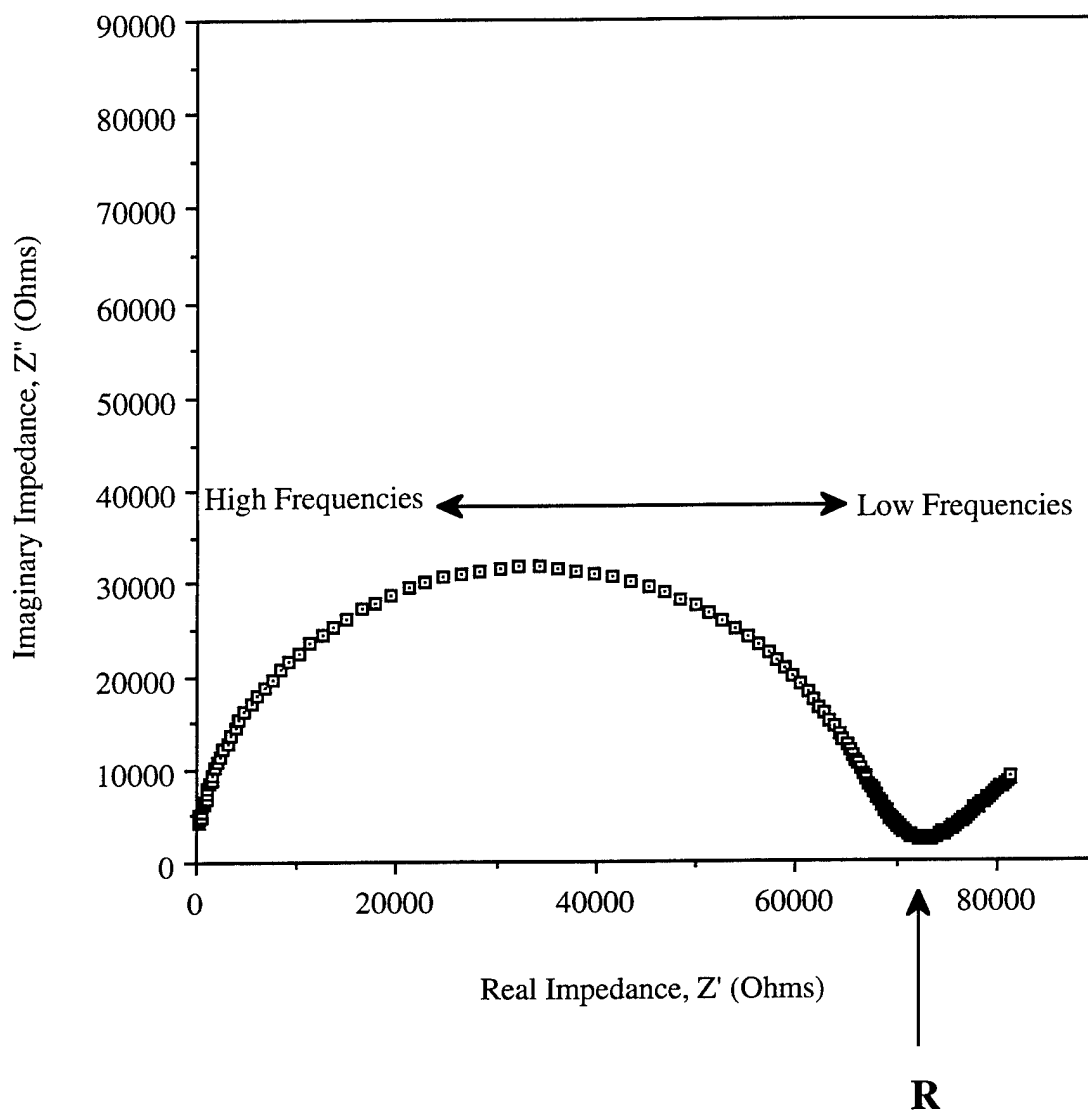


Figure 3: Sample Impedance Plot of Nafion 117 after being exposed to approximately 30% of its dry weight of methanol. R is determined as the lowest point on the graph.

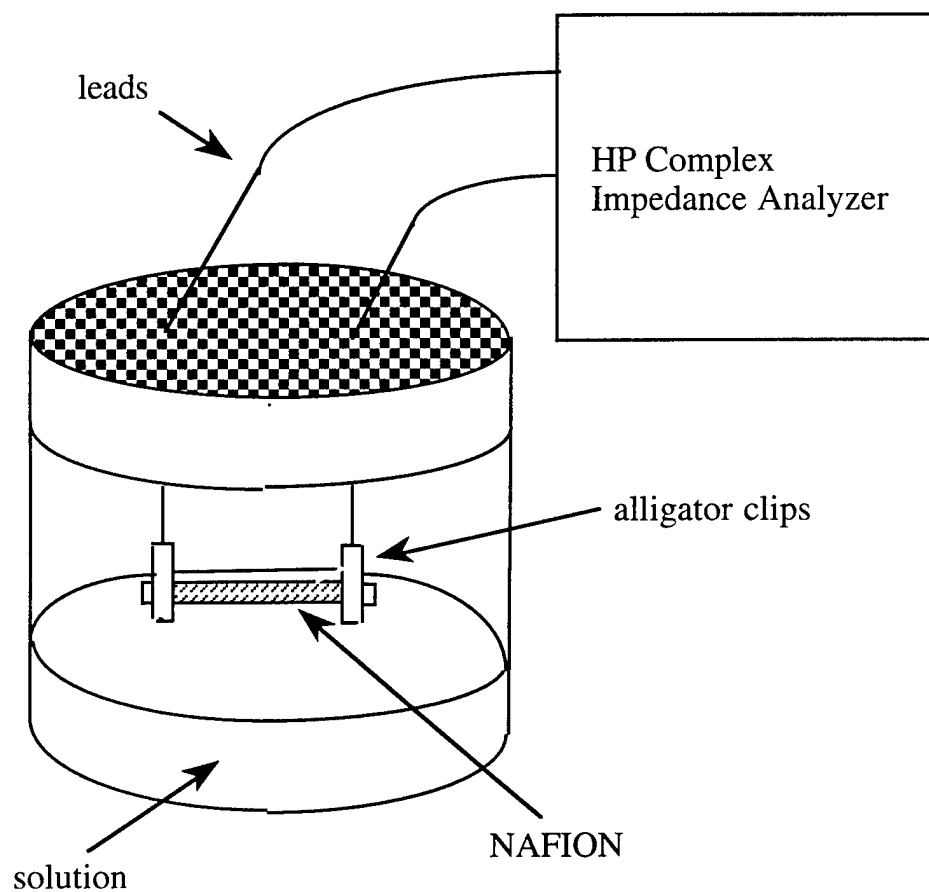


Figure 4: Diagram of the apparatus used to condition the NAFION and measure its complex impedance.



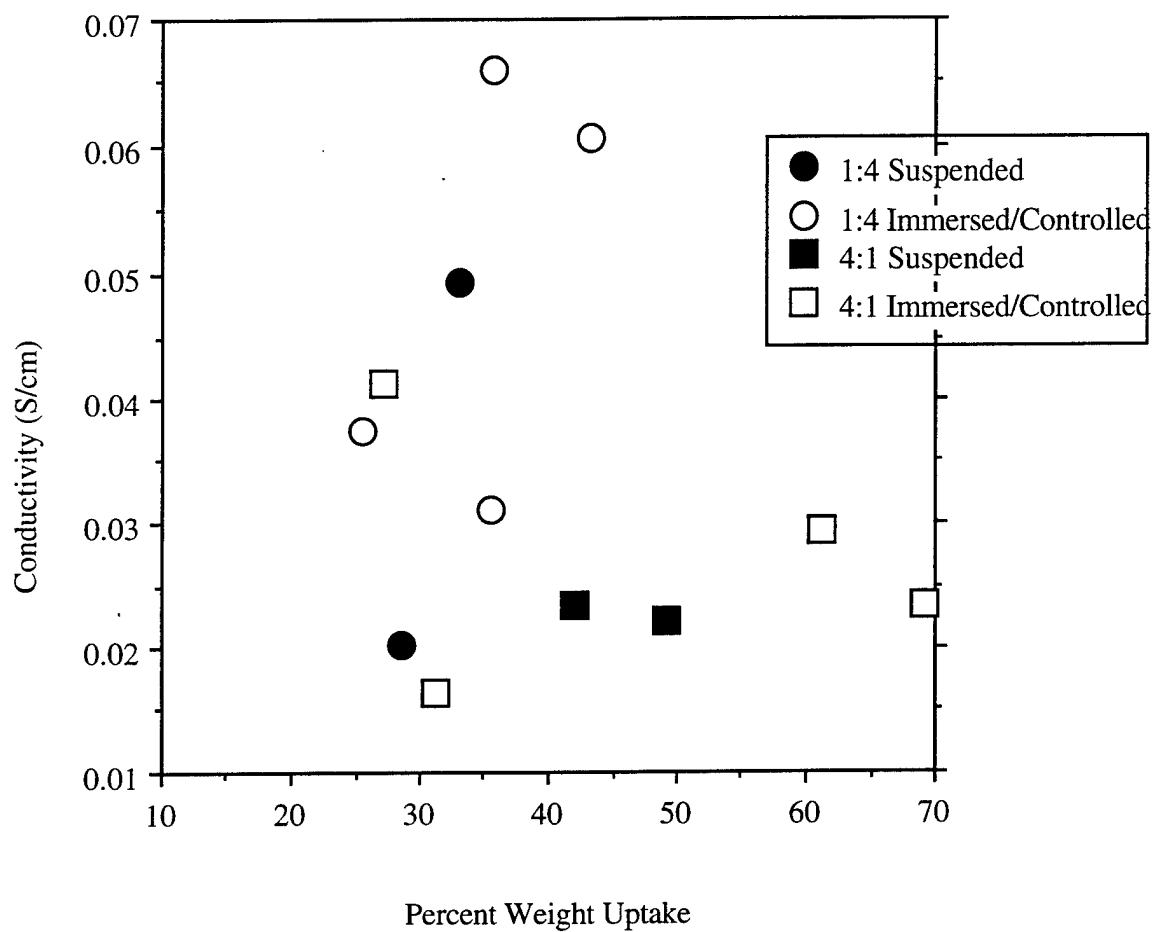


Figure 5: Graph of the conductivity versus the percent weight uptake for different methods of conditioning solutions 1:4 and 4:1.

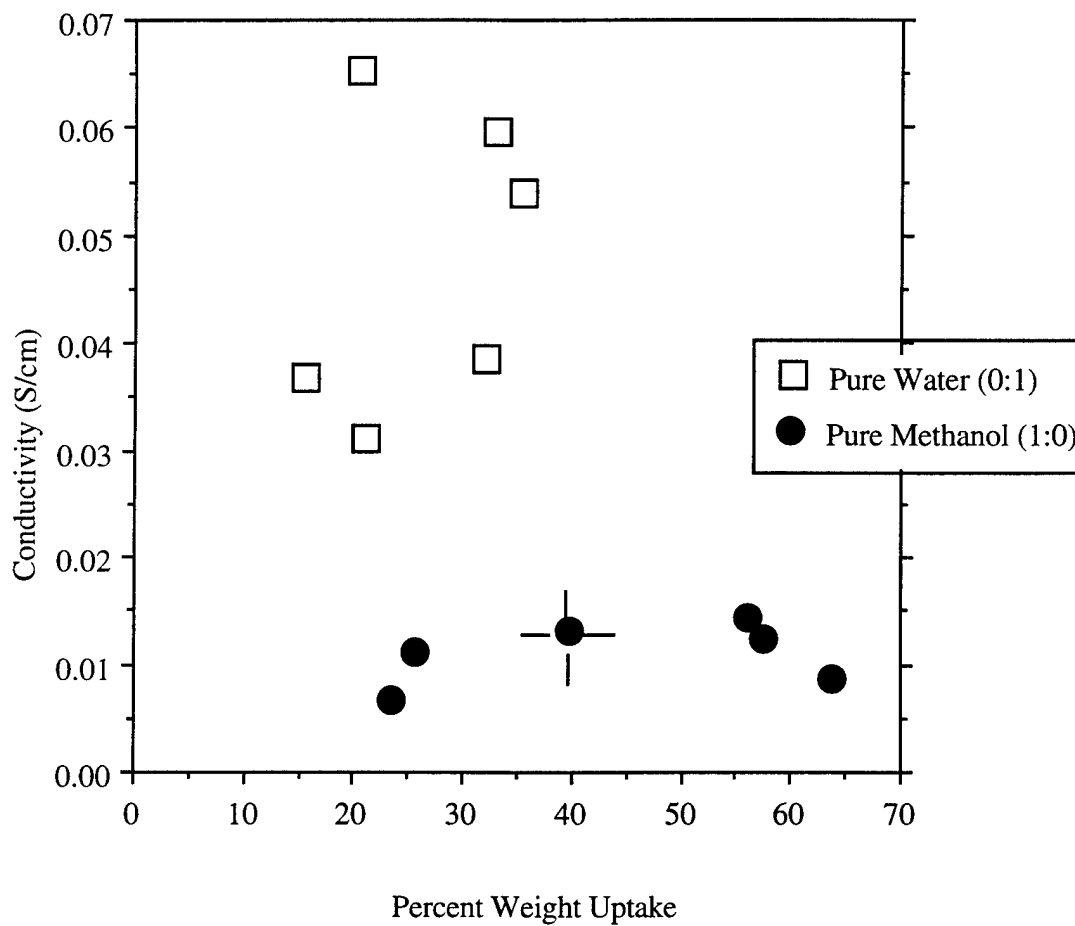


Figure 6: Graph of the weight of solution absorbed by the sample versus the conductivity of the sample. The data is from a pure methanol solution and a pure water solution. A typical uncertainty is shown on one of the points of methanol data.

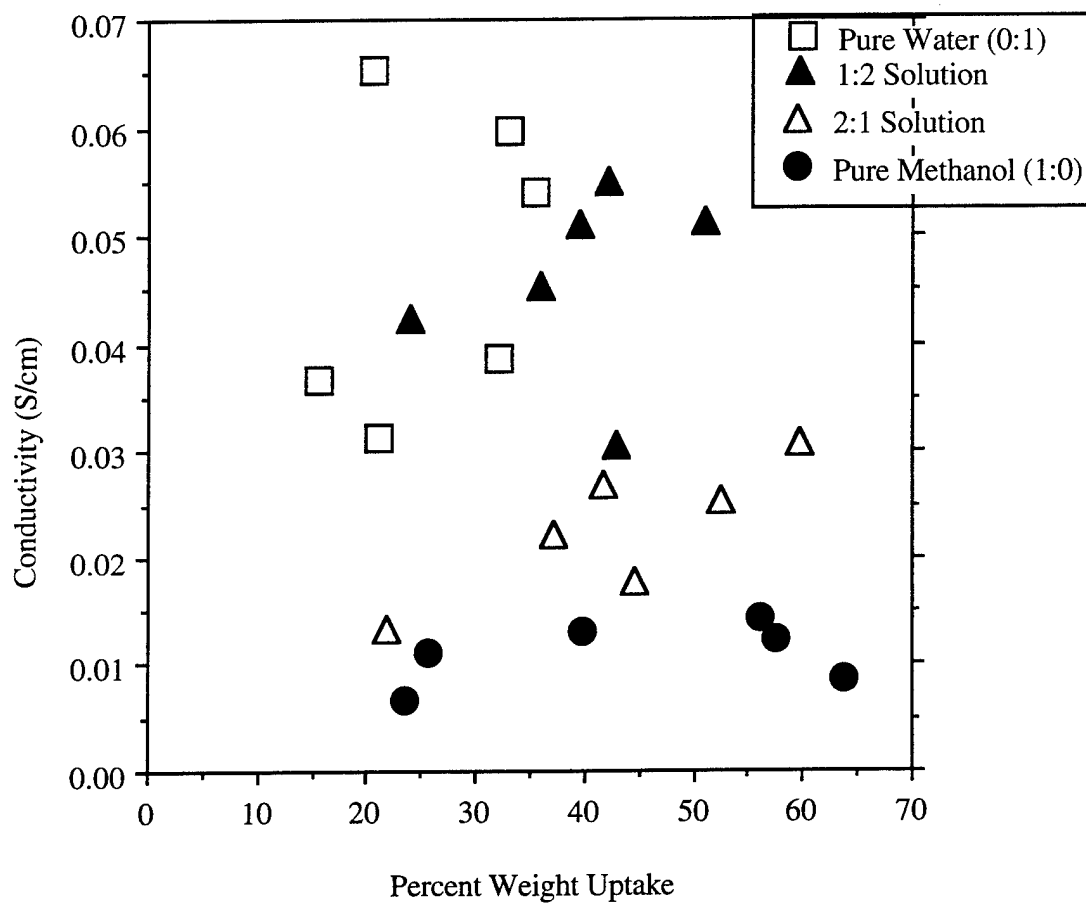


Figure 7: Graph of the weight of solution absorbed by the sample versus the conductivity of the sample. The data is from pure methanol, 2:1, 1:2, and pure water solutions.

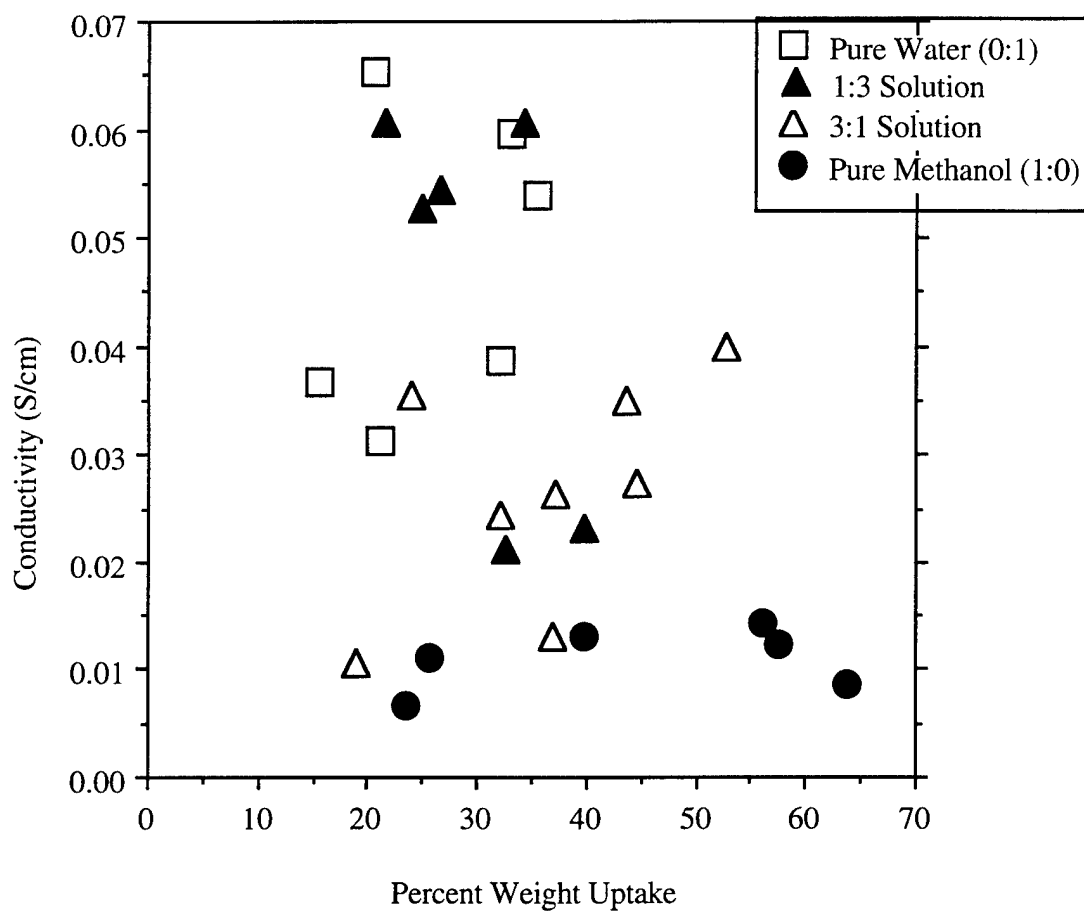


Figure 8: Graph of the weight of solution absorbed by the sample versus the conductivity of the sample. The data is from pure methanol, 3:1, 1:3, and pure water solutions.

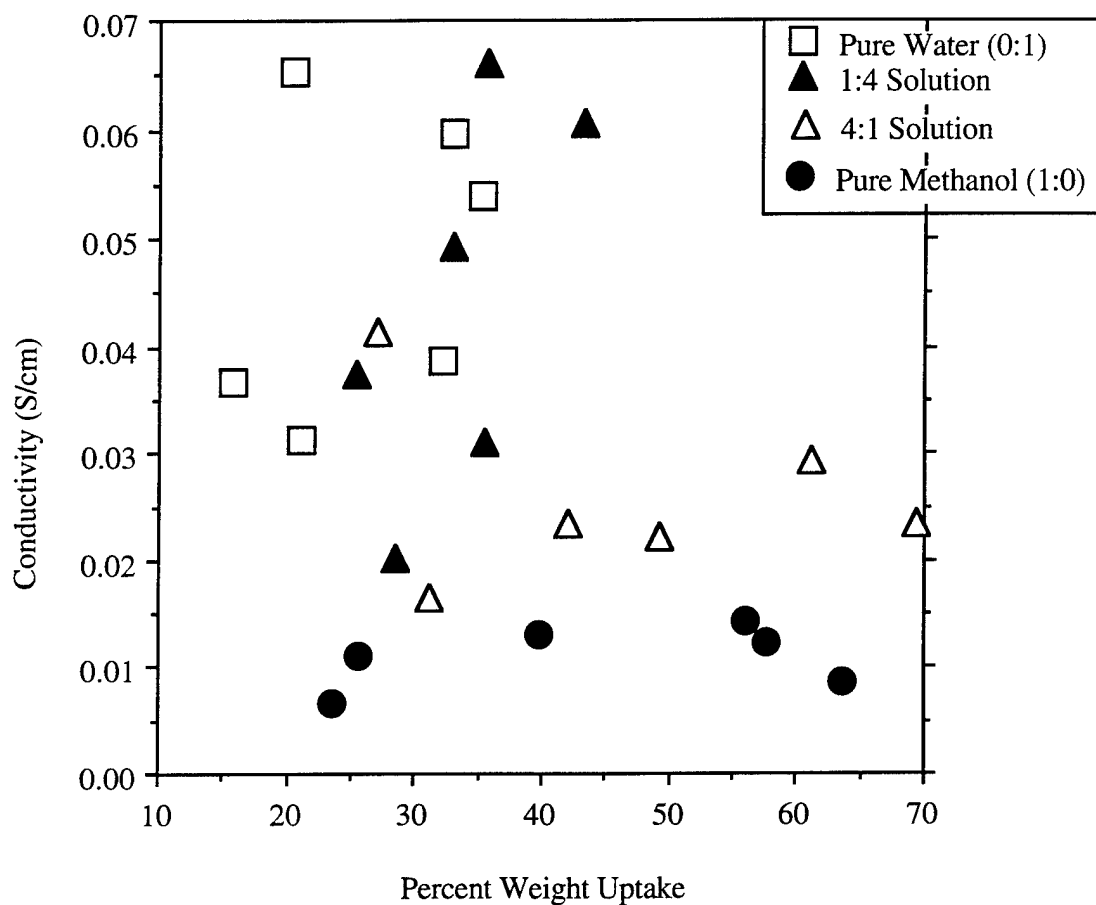


Figure 9: Graph of the weight of solution absorbed by the sample versus the conductivity of the sample. The data is from pure methanol, 4:1, 1:4, and pure water solutions.

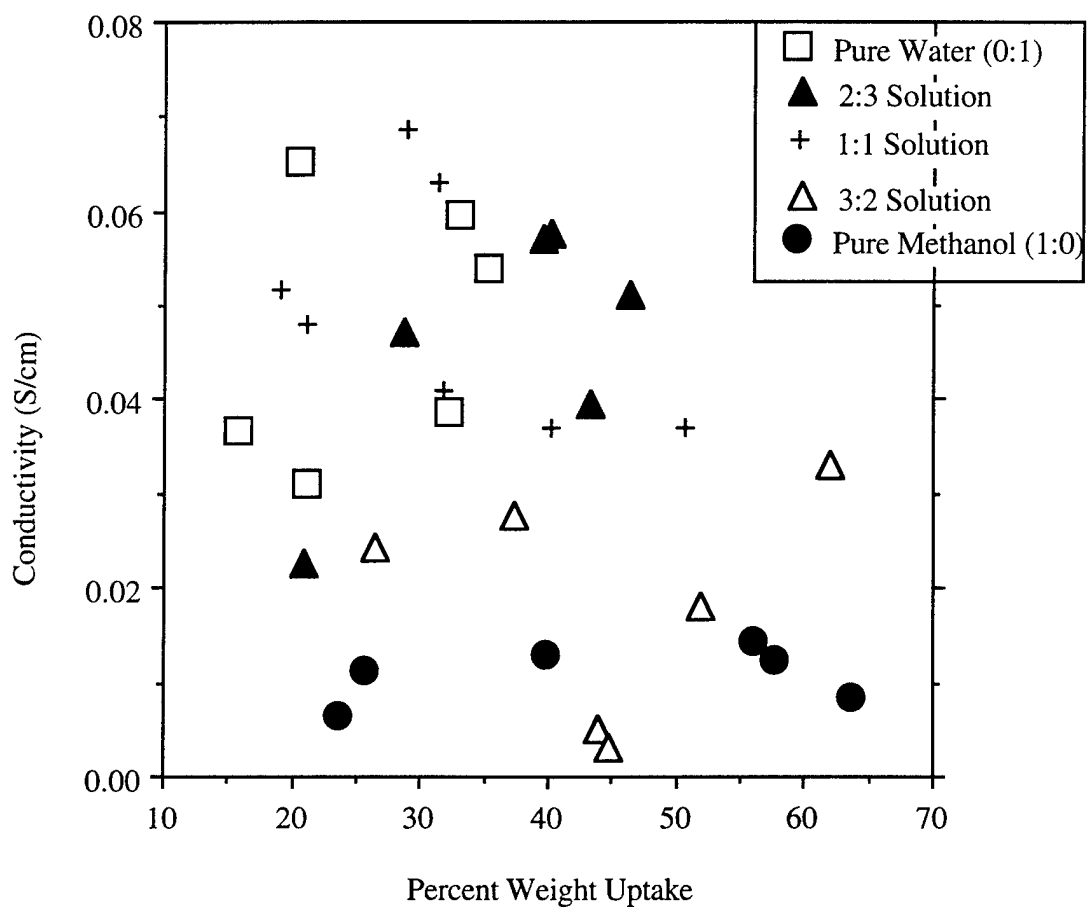


Figure 10: Graph of the weight of solution absorbed by the sample versus the conductivity of the sample. The data is from pure methanol, 3:2, 1:1, 2:3, and pure water solutions.

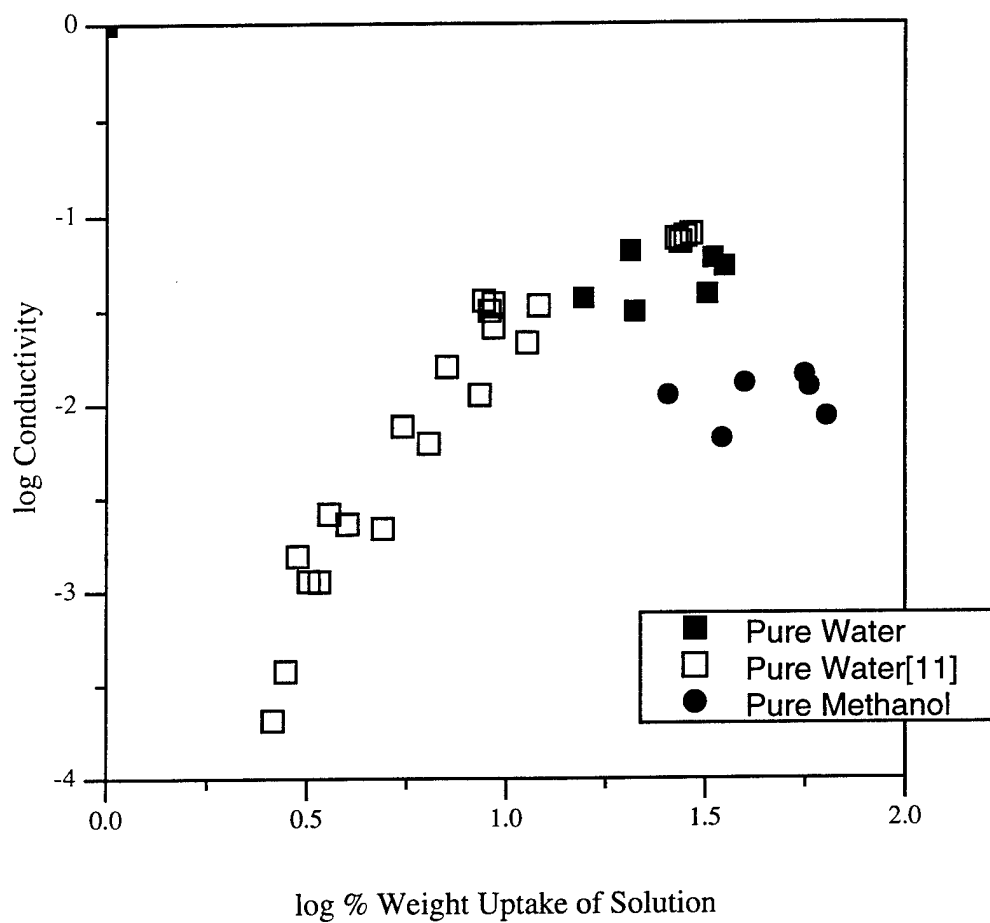


Figure 11: Graph of the log of the amount of solution absorbed by the sample versus the log of the conductivity of the sample. Data is from pure water and pure methanol.

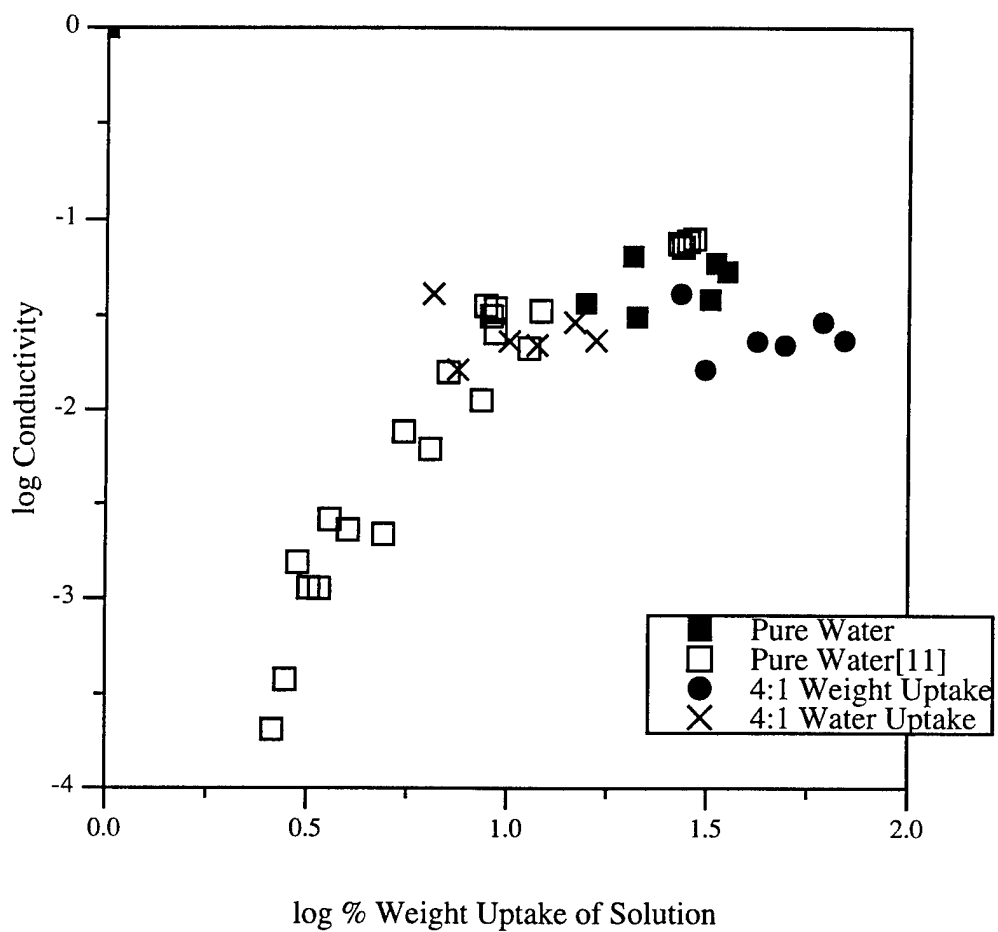


Figure 12: Graph of the log of the amount of solution absorbed by the sample versus the log of the conductivity of the sample. Data is from pure water and 4:1 solution.





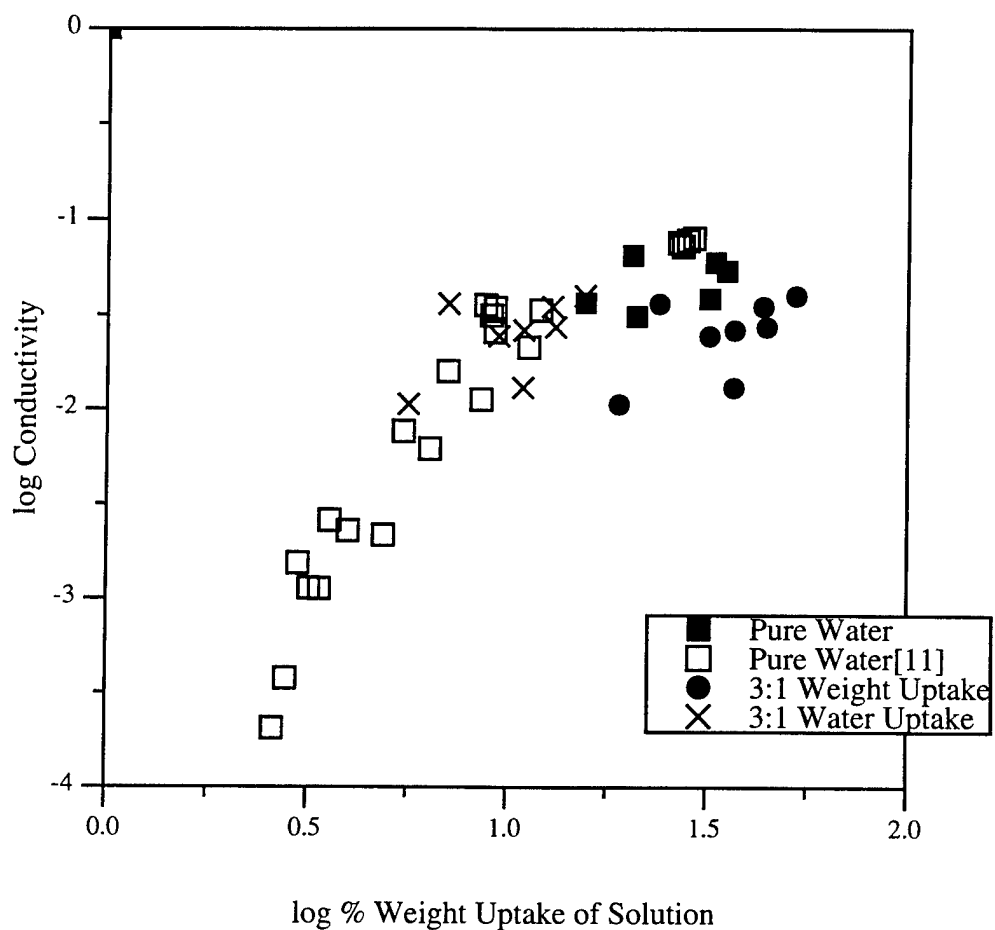


Figure 14: Graph of the log of the amount of solution absorbed by the sample versus the log of the conductivity of the sample. Data is from pure water and 3:1 solution.

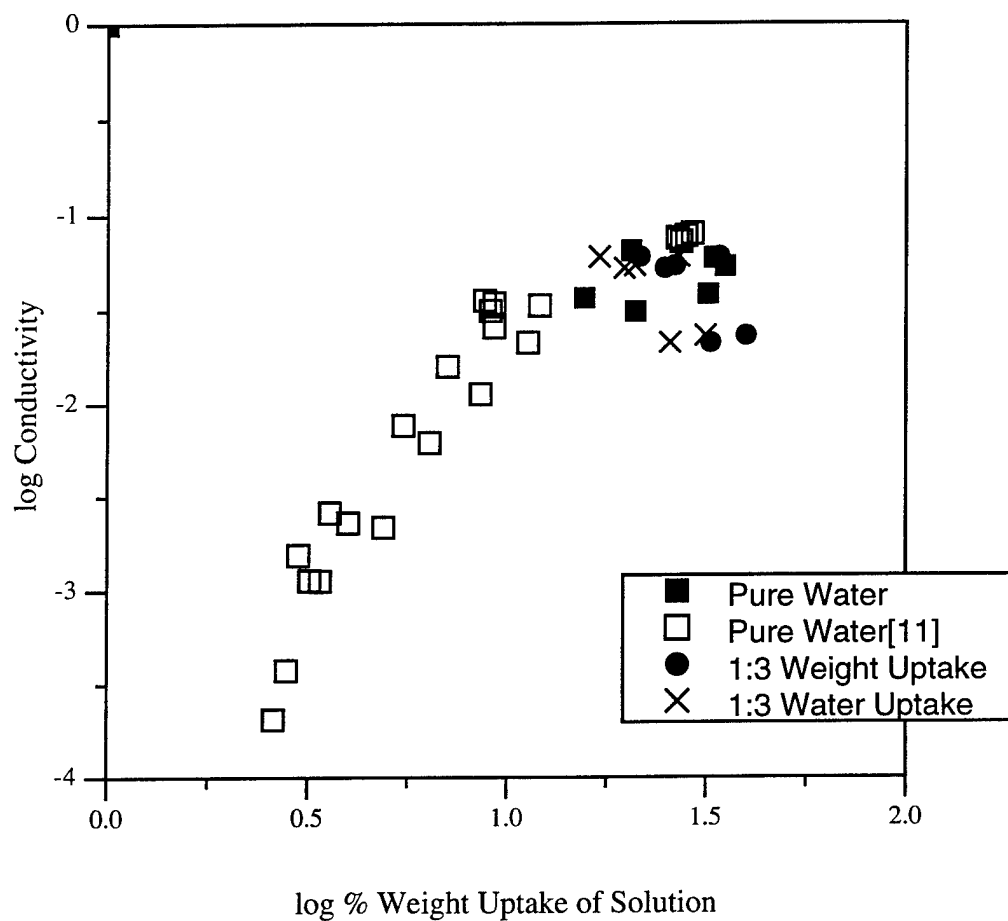


Figure 15: Graph of the log of the amount of solution absorbed by the sample versus the log of the conductivity of the sample. Data is from pure water and 1:3 solution.

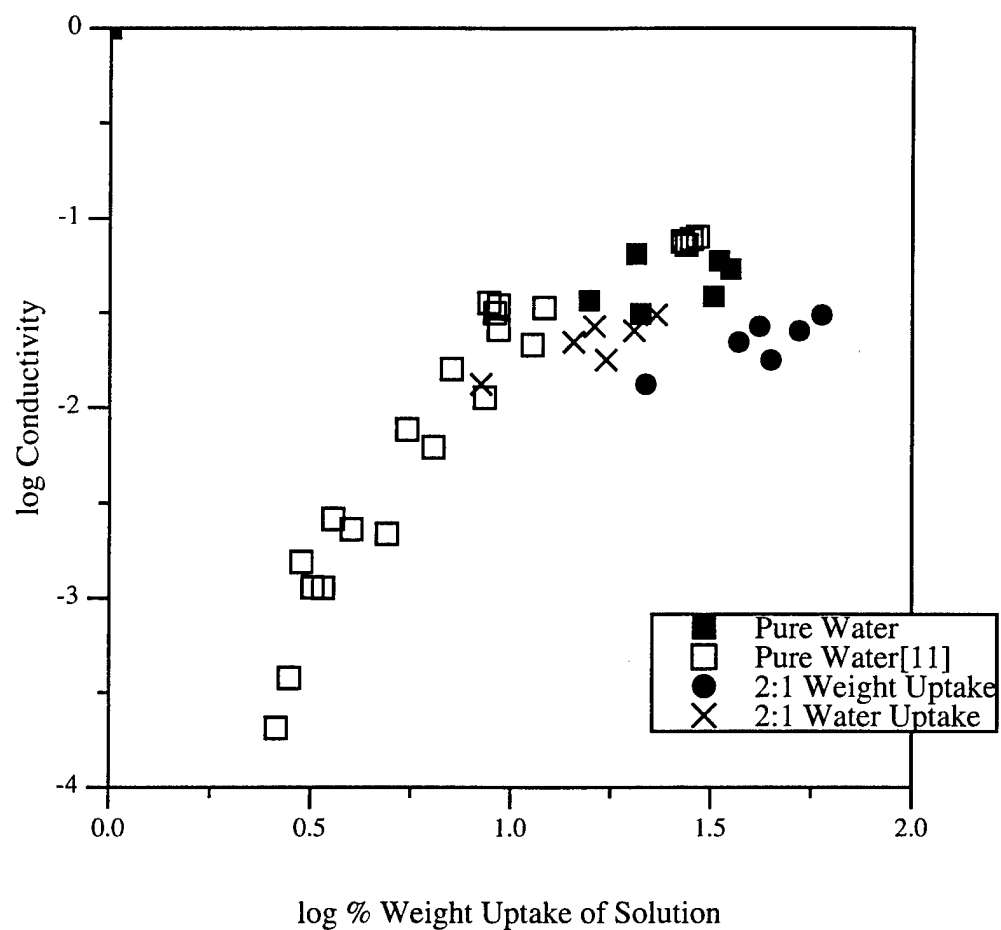


Figure 16: Graph of the log of the amount of solution absorbed by the sample versus the log of the conductivity of the sample. Data is from pure water and 2:1 solution.

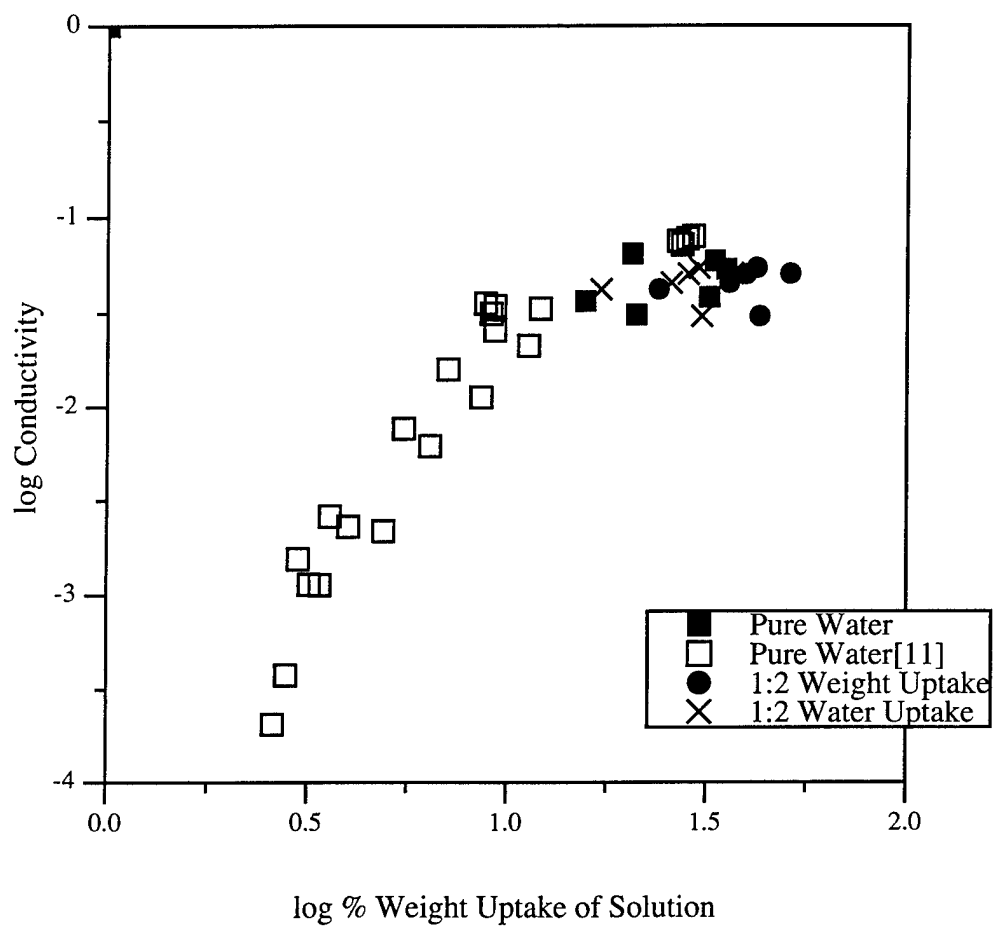


Figure 17: Graph of the log of the amount of solution absorbed by the sample versus the log of the conductivity of the sample. Data is from pure water and 1:2 solution.

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## APPENDIX A- ERROR ANALYSIS

As stated in the main body of the paper, there was a great deal of scatter in the data collected in this project, and therefore a great deal of error inherent in the data points. Here, an error analysis is applied to one data point in an attempt to show the variation possible.

Equation 5 was used to calculate the conductivity of the sample.  $R$  was measured from the complex impedance plot shown in Figure 7 to be 72900 Ohms. The average error here was approximately  $\pm 1500$  Ohms. This error resulted from measuring the x-axis intercept from the graph. The length and width of the sample were measured using digital calipers which created an error of 0.005 cm, where the length was 3.235 cm and the width was .379 cm. The height of the sample was measured using a thickness meter which created an error of 0.0005 with a height of .0178. These values resulted in a conductivity of .0066 S/ cm and an uncertainty of 0.0004 S/cm.

The percent weight uptake was calculated by Equation 7. The initial dry weight of the sample,  $W_i = 0.0585$  gms, had an error of 0.0005 gms. The wet weight,  $W_f = 0.0789$  gms, however, had an additional error which was produced by possible extra moisture remaining on the sample during weighing. This increased its error to 0.001 gms. The percent weight uptake was therefore calculated to be 34.9%, and its uncertainty was 2.5 %.

It must be emphasized that due to the great variation of methods and results, the above calculations are for only one point, and were calculated to show the possible variation in the data. A more exact analysis of the errors inherent in this experiment was not possible, due to the many different factors involved in measurements as stated in Section 4.4.